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Zero-Valent Iron Technical Bulletin

Benefits of Sulfidation



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Summary

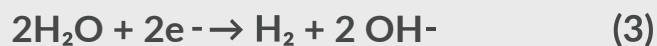
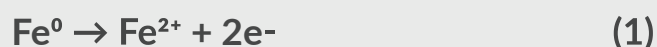
S-MicroZVI[®] is a colloidal sulfidated zero-valent iron (ZVI) product in which the ZVI particles are surface-treated with a reduced sulfur species. This chemical modification of ZVI has been shown to enhance its usefulness for *in situ* groundwater in several ways. Sulfidated iron inhibits the reaction between unmodified ZVI and water, extending the longevity of the amendment. Additionally, sulfidating the zero

valent iron enhances the rate of reduction for common groundwater contaminants such as perchloroethene (PCE) and trichloroethene (TCE). S-MicroZVI also allows 1,1,1-trichloro-ethane (1,1,1-TCA) to be degraded without forming significant quantities of the more toxic daughter product 1,1-dichloroethane (1,1-DCA).

Background

ZVI is a widely-used amendment capable of facilitating the electrochemical reduction of chlorinated contaminants to benign end products (**Equations 1 and 2**). However, the efficiency of ZVI treatments are reduced by the competing reaction with water (corrosion) to produce molecular hydrogen (Equation 3). When ZVI reacts with water, the particle surface becomes passivated with oxide and hydroxide species, and this corrosion of the surface limits further reaction between the ZVI and the targeted contaminants. Thus, the development of ZVI materials that react preferentially with target contaminants over water is desirable.

The benefits of using sulfidated ZVI have been realized for over twenty years¹ and a recent comprehensive review² and other detailed research studies have contributed to a renewed



Electrochemical Reduction of chlorinated contaminant equations

interest in sulfidated ZVI. A key finding of these studies^{3,4} is that the reactivity of ZVI with water can be drastically reduced by sulfidating the ZVI. ZVI sulfidation forms iron sulfides (FeS) at the particle surface that favor the degradation of contaminants rather than the reduction of water,⁵ thereby improving the longevity of the ZVI. In addition to improving the longevity, sulfidating ZVI also affects the kinetics, mechanisms, and reaction products, as summarized by Fan, et al.²

Background - Continued

S-MicroZVI transfers the established benefits of sulfidated ZVI to an easily-injectable colloid designed for the *in situ* remediation of soil and groundwater. S-MicroZVI features particles of ZVI that are encapsulated with iron sulfide (Figure 1).

PCE and TCE are degraded more rapidly by S-MicroZVI than by unsulfidated ZVI. Furthermore, S-MicroZVI offers mechanistic advantages for the degradation of contaminants such as 1,1,1-TCA. Studies conducted in our laboratory confirmed the findings of Fennelly et al., which showed the degradation of 1,1,1-TCA to 1,1-DCA by unsulfidated ZVI.⁶ 1,1-DCA is more toxic than its parent compound, and while 1,1-DCA can be degraded by ZVI, the degradation rate is slow. When treated with S-MicroZVI 1,1,1-TCA is instead degraded to

benign end products without generating significant quantities of 1,1-DCA. This is consistent with previously published results suggesting that 1,1,1-TCA can be directly reduced to ethane and ethene via a series of radical and carbenoid intermediates.⁶

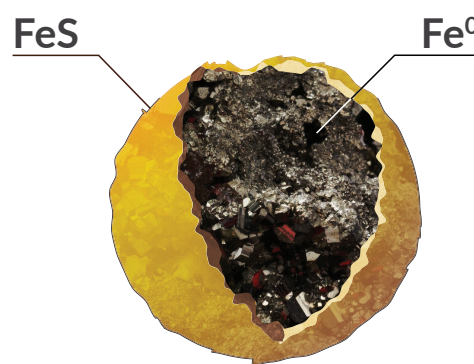


Figure 1. S-MicroZVI consists of ZVI particles that are coated with iron sulfide.

Study Demonstrating the Longevity of S-MicroZVI

Study Objective

The objective of this study was to demonstrate that S-MicroZVI has greater longevity than unsulfidated ZVI.

Experimental Setup

Studies were performed in 8-oz amber bottles with Mininert™ caps. The total volume for each sample was 230 mL. Triplicate samples were

prepared for each of the three conditions described below in 50 mM HEPES buffer (pH 7) with 20 g sandy loam.

- **PCE control:** Untreated samples containing only sandy loam and HEPES buffer.
- **Unsulfidated ZVI:** Samples treated with unsulfidated colloidal ZVI at a concentration of 4 g/L as ZVI.
- **S-MicroZVI:** Samples treated with S-MicroZVI at a concentration of 4 g/L as ZVI.

Study Demonstrating the Longevity of S-MicroZVI - Continued

PCE (1.4 μ L, corresponding to a concentration of 10 mg/L) was spiked into each bottle at one-week intervals, and the contaminant concentrations were monitored by GC-MS. The reported values are averages of the triplicate samples.

Results & Discussion

The degradation of PCE by unsulfidated ZVI and S-MicroZVI was observed over a period of 42 days with 6 spikes of PCE. The data are presented in Figure 2. After approximately 2 weeks, PCE began accumulating in the unsulfidated ZVI-

samples, and the reactivity of the unsulfidated ZVI began to differentiate from that of S-MicroZVI. S-MicroZVI maintained its reactivity for the duration of the experiment. After 42 days, 58 % of PCE had been removed from solution in the sample treated with unsulfidated ZVI, and 92 % of PCE had been removed from the sample treated with S-MicroZVI. Percentages were calculated relative to the PCE control. The results of this study indicate that while both unsulfidated ZVI and S-MicroZVI degrade PCE, S-MicroZVI showed greater reactivity and longevity.

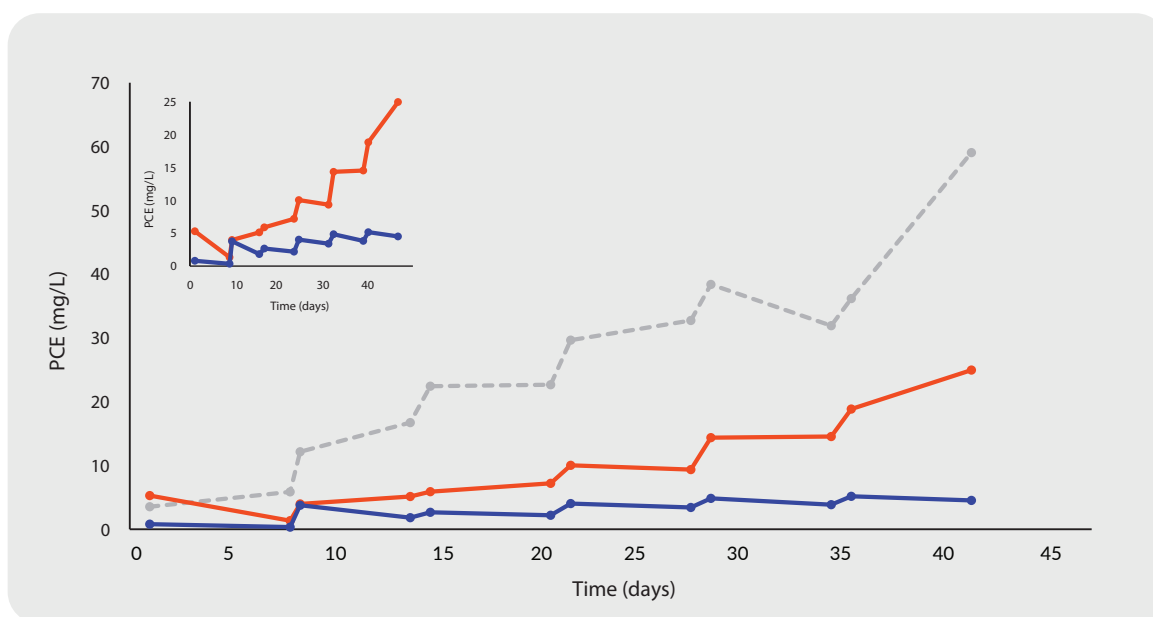


Figure 2. Aqueous sample concentrations of PCE in control **Untreated** --- **Unsulfidated ZVI** — **S-MicroZVI** — The inset graph shows the same data zoomed in to better illustrate the difference in reactivity between unsulfidated ZVI and S-MicroZVI.

Study Demonstrating Increased Reactivity with S-MicroZVI

Study Objective

The objective of this study was to demonstrate that S-MicroZVI degrades TCE more rapidly than unsulfidated ZVI.

Experimental Setup

Reactivity was evaluated in 8-oz bottles by adding 200 g of sand, 80 g of buffer (50 mM HEPES, pH 7), and 2 μ L of TCE (37 mg/L aqueous phase concentration). Bottles were dosed with either 2 g/L S-MicroZVI (ZVI basis), 10 g/L carbonyl iron ($\sim 4 \mu$ m particle size), or 10 g/L microscale ZVI ($\sim 40 \mu$ m particle size).

Results and Discussion

The concentration of TCE was measured over time by GC-ECD. Pseudo-first-order rate constants were determined from the slope of a graph showing $\ln [\text{TCE}]$ vs. time. Analysis of the mass-adjusted rate constants showed that the reactivity of S-MicroZVI was 28 times that of unsulfidated ZVI (**Table 1**). This rate enhancement is comparable to previously published results with nanocrystalline and microscale ZVI.⁴

Material (particle size)	Dose (g/L)	Rate Constant (day ⁻¹)	Mass Adjusted Rate Constant (L g ⁻¹ day ⁻¹)
S-MicroZVI (2-3 μ m)	2.0	0.56	0.28
Carbonyl iron (4 μ m)	10	0.10	0.01
Microscale ZVI (<44 μ m)	10	0.10	0.01

Table 1. Kinetic data showing pseudo-first-order rate constants for the degradation of TCE by S-MicroZVI, carbonyl iron, and microscale ZVI. The dose of carbonyl iron and microscale ZVI is 10 g/L as ZVI rather than 2 g/L so that the degradation of TCE occurs at a rate that can be observed during the timeframe of the experiment.

Study Demonstrating the Benefits of S-MicroZVI for the Degradation of 1,1,1-TCA

Study Objective

The objective of this study was to demonstrate that less of the toxic daughter product 1,1-DCA is produced when 1,1,1-TCA is degraded by S-MicroZVI rather than unsulfidated ZVI.

Experimental Setup

Batch studies were performed in 8-oz amber bottles with Mininert™ caps. The total volume of each sample was 230 mL. Triplicate samples were prepared for each of the three conditions described below in 50 mM HEPES buffer (pH 7) with a contaminant concentration of 75 µM 1,1,1-TCA (10 mg/L).

- **1,1,1-TCA control:** Untreated samples containing only HEPES buffer.
- **Unsulfidated ZVI:** Samples treated with commodity carbonyl iron at a concentration of 10 g/L.
- **S-MicroZVI:** Samples treated with S-MicroZVI at a concentration of 10 g/L as iron.

Results and Discussion

The degradation of 1,1,1-TCA is illustrated in Figure 3. The 1,1,1-TCA control (represented by the black dashed line) shows no loss of contaminant. 1,1,1-TCA is represented by the green line in the treated samples containing unsulfidated ZVI (Figure 3A) or S-MicroZVI (Figure 3B). In both treated samples, 1,1,1-TCA is removed from solution. However, while unsulfidated ZVI converts 1,1,1-TCA to 1,1-DCA (gray line, Figure 3A), minimal formation of 1,1-DCA is observed in the sample treated with S-MicroZVI (Figure 3B).

This study clearly illustrates the difference in degradation pathways between S-MicroZVI and unsulfidated ZVI. Unsulfidated ZVI rapidly degrades 1,1,1-TCA to 1,1-DCA via reductive elimination, but the degradation stalls at 1,1-DCA. Alternatively, S-MicroZVI degrades 1,1,1-TCA without generating of significant quantities of 1,1-DCA.

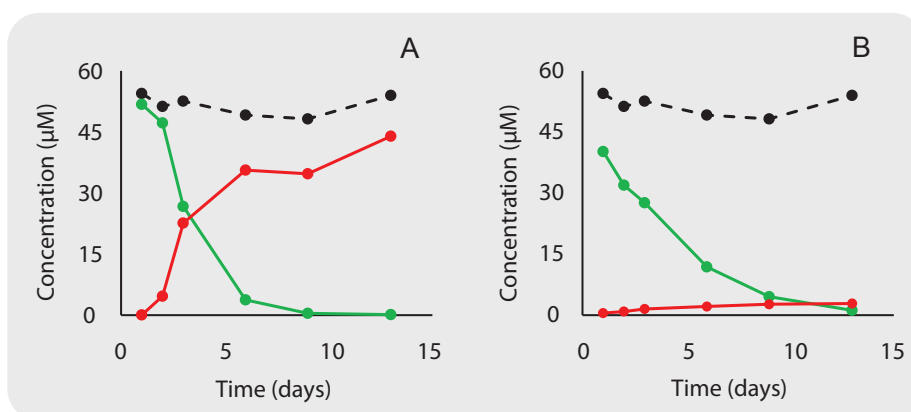


Figure 3. Aqueous concentrations of chlorinated ethanes in samples treated with A) unsulfidated ZVI and B) S-MicroZVI. 1,1,1-TCA control (no ZVI) --- 1,1,1-TCA — 1,1-DCA —

Conclusions

The benefits of sulfidated ZVI have been extensively documented, and S-MicroZVI was engineered to provide the benefits of sulfidated ZVI in an easily injectable technology for soil and groundwater remediation. S-MicroZVI demonstrates excellent longevity and favors the degradation of contaminants over the reduction of water. S-MicroZVI provides kinetic and mechanistic

advantages as well. Our studies show that S-MicroZVI reacted 28 times faster with TCE than does unsulfidated ZVI. The mechanistic advantages of S-MicroZVI are clearly observable when degrading 1,1,1-TCA, as significantly lower concentrations of 1,1-DCA are formed than when degrading 1,1,1-TCA is degraded using unsulfidated ZVI.

References

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